

STUDIES OF DIESEL FUEL INSOLUBLES FORMATION AND FUEL STABILIZER ADDITIVES

**INTERIM REPORT
BFLRF No. 255**

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Under Contract to

**U.S. Army Belvoir Research, Development
and Engineering Center
Materials, Fuels and Lubricants Laboratory
Fort Belvoir, Virginia**

AD-A202 297

Contract No. DAAK70-87-C-0043

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REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS None										
2a. SECURITY CLASSIFICATION AUTHORITY N/A		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited										
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE												
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Interim Report BFLRF No. 255		5. MONITORING ORGANIZATION REPORT NUMBER(S)										
6a. NAME OF PERFORMING ORGANIZATION Belvoir Fuels and Lubricants Research Facility (SwRI)	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION										
6c. ADDRESS (City, State, and ZIP Code) Southwest Research Institute San Antonio, Texas 78284		7b. ADDRESS (City, State, and ZIP Code)										
8a. NAME OF FUNDING/SPONSORING ORGANIZATION U.S. Army Belvoir Research, Development and Engineering Center	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER DAAK70-85-C-0007; DAAK70-87-C-0043, WD 9										
8c. ADDRESS (City, State, and ZIP Code) Fort Belvoir, VA 22060-5606		10. SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO. 61102 PROJECT NO. 1T161102 TASK NO. AH51 WORK UNIT ACCESSION NO. FF(2)										
11. TITLE (Include Security Classification) Studies of Diesel Fuel Insolubles Formation and Fuel Stabilizer Additives (U)												
12. PERSONAL AUTHORIS Westbrook, Steven R.; Stavinoha, Leo L.; and Present, David L.												
13a. TYPE OF REPORT Interim	13b. TIME COVERED FROM Oct 86 TO Aug 88	14. DATE OF REPORT (Year, Month, Day) 1988 August	15. PAGE COUNT 27									
16. SUPPLEMENTARY NOTATION												
17. COSATI CODES <table border="1"><tr><th>FIELD</th><th>GROUP</th><th>SUB-GROUP</th></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr></table>		FIELD	GROUP	SUB-GROUP							18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Diesel Fuels Deteroration Particulates Fuel Additives Models Stability Inhibitors	
FIELD	GROUP	SUB-GROUP										
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Insolubles in diesel fuels are known to occur through several mechanisms, some of which include polymerization, condensation, and acid-base reactions. Recent studies have revealed that acid-base reactions (or acid-catalyzed reactions) are especially important in the formation of sediments in fuels containing catalytically cracked stock. Evidence also exists that simply removing the acid and base fractions of the fuel does not completely eliminate sediment formation, which would indicate some sort of preliminary reaction, such as oxidation. Fuels containing little or no cracked stock are usually subject to different reactions to form insolubles. The type of additive used to reduce insolubles formation depends on the reactions that occur to produce the insolubles. For these reasons, additive efficacy will vary between fuels.												
(Cont'd)												
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION Unclassified										
22a. NAME OF RESPONSIBLE INDIVIDUAL Mr. Tom Bowen		22b. TELEPHONE (Include Area Code) (703) 664-3576	22c. OFFICE SYMBOL STRBE-VF									

19. ABSTRACT (Cont'd)

During this study, the formations of fuel insolubles in a straight run fuel, a light cycle oil, and a blend of the two were studied. The test fuels were stored at 80°C for periods up to 28 days. The effects of several commercial fuel stabilizer additives and one pure compound on sediment formation were also studied. The fuels and fuel sediments were analyzed, and the results were used to develop a model system. Studies of the formation of insolubles during the aging of the model system showed the importance of acids in sediment formation. The inhibition mechanism of one fuel stabilizer, N,N'-dimethylcyclohexylamine, was also studied. The usefulness of the model system for evaluating stabilizer additive effectiveness was also demonstrated. (A.W.)

FOREWORD

This work was conducted at the Belvoir Fuels and Lubricants Research Facility (SwRI) located at Southwest Research Institute (SwRI), San Antonio, TX under Contract Nos. DAAK70-85-C-0007 and DAAK70-87-C-0043 during the period October 1986 through August 1988. The work was funded by the U.S. Army Belvoir Research, Development and Engineering Center, Ft. Belvoir, VA, with Messrs. F.W. Schaekel and T.C. Bowen (STRBE-VF) as the Contracting Officer's representatives and Mr. M.E. LePera, Chief of Fuels and Lubricants Division (STRBE-VF), as the project technical monitor.

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ACKNOWLEDGMENTS

The authors gratefully acknowledge the assistance of William McMahon, Charles Nystrom, James Herrera, Sherry Douvry, Cindy Sturrock, Jim Pryor, and Janet Buckingham in their efforts on this project.

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I. INTRODUCTION

The stability of middle distillate fuels during storage is an important consideration for both military and commercial users. Deterioration products can cause deposits that, in turn, lead to filter and injector nozzle plugging.^{(1)*} The requirement for stable fuel is especially critical in those situations in which the fuel may remain in storage for long periods of time, for example, military use.⁽²⁾ Often the best way to increase the storage stability of the fuel is through the use of additives. However, the results obtained with a particular additive will depend on several factors, including the type of fuel (i.e., gasoline, diesel, or jet), the crude source, the refining processes, and the storage environment.^(3,4)

The chemical composition of diesel fuel deterioration products and the reactions that form them have been studied for many decades. The compounds most often identified with the formation of these fuel sediments are those containing nitrogen and sulfur. For this reason, many investigations of diesel fuel stability have centered around the contribution of these compounds to the formation of fuel-insoluble sediments. Certain alkyl pyrroles, most notably 2,5-dimethylpyrrole (DMP), have long been known to promote sediment formation in middle-distillate fuels.⁽⁵⁾ However, more recent work has shown that alkyl indoles play a greater role in the formation of diesel fuel deterioration products than do the alkyl pyrroles.^(6,7) This increased role is due to the greater relative concentration of the indoles in diesel fuel as compared with the pyrroles. Sulfur-containing aromatic compounds, especially thiols and sulfonic acids, are also known to promote sediment formation in diesel fuels.⁽⁸⁻¹⁰⁾ The effect of these sulfur-containing compounds was shown to be primarily related to the acidity of the sulfonic acids; the thiols participate primarily through first being oxidized to sulfonic acids.⁽¹¹⁾

The majority of past research on diesel fuel degradation has been conducted on actual fuels. This method provides realistic sediments; however, analysis of these sediments and the reactions that form them are complicated by the numerous chemical species found in most diesel fuels. Some researchers have selectively removed and/or added known compounds and observed the results. Powers and Wotring showed that No. 2 grade fuel oils could be stabilized by caustic treating to remove acidic components.⁽¹²⁾

* Underscored numbers in parentheses refer to the list of references at the end of this report.

Hiley and Pedley confirmed this observation and also found that instability could be restored through the addition of sulfonic acids.⁽¹⁰⁾

Much research on fuel degradation has also been conducted using model systems. Frankenfeld studied the formation of sediments using 2,5-dimethylpyrrole in model systems.⁽⁵⁾ Hiley and Pedley studied the effects of storage of several nonbasic, nitrogen compounds in model systems.⁽¹³⁾ Studies of fuel degradation using model systems offer an advantage because they allow for more detailed study of the reactions, and they simplify the analysis of products. However, BFLRF concurs with Hiley and Pedley⁽¹⁰⁾ that an important part of fuel stability studies is to establish that sediments formed artificially, or in model systems, are the same or closely related to sediments that form during the aging of actual fuel.

The purposes of the work described herein were: 1) to analyze sediments formed from the aging of diesel fuels to determine the predominate species present, 2) based on the results of sediment analyses, develop a model system that more closely resembles an actual fuel and produces "realistic" sediments, and 3) use this model system to study fuel degradation and additive-inhibition mechanisms.

II. EXPERIMENTAL

A. Fuels

Two fuels were used in this study. The first fuel was a Reference No. 2 diesel fuel (Cat 1-H) obtained from a central Texas refinery. This fuel contained no cracked stocks or stabilizer additives. The second was a 100-percent light-cycle oil (LCO) feed stock obtained from a Texas gulf coast refinery. TABLE I lists characterization data for these two fuels. Unused fuel was stored at 40°C (40°F) under argon blanket.

B. Fuel Preparation and Aging

All fuels were aged at 80°C (176°F) in borosilicate glass bottles. The square-shape bottles with straight sides had an approximate volume of 125 milliliters (mL). A total of 100 mL of fuel was placed in each bottle for aging. During aging, the bottles were

TABLE 1. Characterization Data for Test Fuels

Parameter	Cat I-H	LCO
Gravity, API, 60°F	34.1	17.2
Distillation, D 86°, °F(°C)		
50% evap	525(274)	548(287)
90% evap	612(322)	654(346)
End Point	660(349)	695(368)
Color, D 1500	1.5	3.0
Sulfur, XRF, mass%	0.41	0.65
Nitrogen, wt%	—	0.096
Total Acid No., D 664, mg KOH/gm	0.026	0.05
Carbon Residue, 10% Bottoms, wt%	0.10	0.19
Particulate Contamination, D 2276, mg/L	3.0	1.1
Accelerated Stability, D 2274, Total Insolubles, mg/100 mL	0.5	0.6
Hydrocarbon Types, FIA, vol%		
Saturates	67.5	16.8
Olefins	2.0	1.9
Aromatics	30.5	81.3
Phenols, wt%	0.0074	0.024
Thiophenols, wt%	<0.00005	0.007

sealed with a vented, screw-top fitted with a polytetrafluoroethylene (PTFE) liner. The fuel samples were aged in an explosion-proof oven. All samples were protected from light before, during, and after aging.

Three commercially available fuel additives and one pure compound were used in this work. They were:

- Additive A - a detergent/dispersant additive. Addition was made at a concentration of 30 parts per million (ppm).
- Additive B - a multi-functional additive containing a rust inhibitor, dispersant, antioxidant/stabilizer, color stabilizer, and metal deactivator. Addition was made at a concentration of 71 ppm.
- Additive C - the antioxidant/stabilizer component of Additive B. Addition was made at a concentration of 30 ppm.

- DMCA - N-N' dimethylcyclohexylamine. This material is the primary component of Additive C (confirmed by gas chromatography/mass spectroscopy). Addition was made at a concentration of 30 ppm.

C. High-Resolution Gas Chromatography/Mass Spectroscopy (GC/MS)

A gas chromatograph, with a fused silica capillary column and a split-splitless capillary injector, was coupled to a mass selective detector (MSD). The MSD produces mass spectra and ion chromatograms of compounds eluting from the high-resolution gas chromatograph (GC). The controller/work station provided high-speed data acquisition at scan rates higher than 1500 amu/sec to assure high resolution of fast peaks. The stored fragmentation patterns were compared with reference mass spectra stored in the work station. The spectra library contains the spectra of 38,791 compounds. The accumulated spectra were also transferred to a minicomputer for storage and further analysis. The minicomputer houses a library containing the spectra of 80,000 compounds and software to perform probability based matching (PBM) and analysis of unknown compounds. TABLE 2 contains a listing of the instrument conditions.

D. Reagents

TABLE 3 lists the reagents used in this study, along with their purity.

E. Sample Workup

Unless otherwise noted, all aged samples were first allowed to equilibrate to room temperature in the dark. Each sample was then filtered under vacuum through two sandwiched, preweighed, glass fiber filters of 0.7- μ m pore size. The filtered fuel was tested for color by ASTM Method D 1500; it was then removed from the filtration flask and stored in a bottle, protected from light. The aging bottle was rinsed three times with filtered isooctane, and the rinsings were poured through the filter. The filter was then rinsed a final time to remove last traces of fuel, removed from the filter support assembly, oven dried (90°C), and reweighed to determine the amount of filterable insolubles. The aging containers were then rinsed with three portions of gum solvent (equal amounts of toluene, acetone, and methanol) (TAM) to remove adherent insolubles from the sides of the glass. A rubber policeman was used, in some instances, to remove

TABLE 2. GC/MS Instrument Settings

<u>GC Conditions</u>	
Description	50 meter x 0.2 mm ID SE-54 Fused Silica, Open Tubular Column
Flow Rate	1.0 cc/min nominal helium
Split Ratio	100:1
Injector Temperature, °C	300
<u>Oven</u>	
Temperature, °C	0
Equilibration Time, min	2
Temperature Program Rate	6°C/min
Final Temperature, °C	300
Final Time, min	10
GC/MSD Interface Temperature, °C	280
<u>MSD Conditions</u>	
Solvent Delay	0.00
eM Volts	0 relative
Resulting Voltage	2200
Start Time	0.00
Low Mass	10.0
High Mass	450.0
Scan Threshold	10
a/d Samples (2 ⁿ)	2
Scans per Second	0.97

TABLE 3. List of Reagents

Name	Purity
n-Dodecane	99 mol%
n-Butylbenzene	99 mol%
α-Methyl Naphthalene	Purified thru silica gel
1-Octadecene	98.6% min
Indole	99+%
2-Methyl Indole	98%
Benzoic Acid	Primary Standard
p-Phenylphenol	99+%
Quinoline	Reagent Grade
1-Butanol	Reagent Grade
2-Naphthalene Sulfonic Acid	Tech (70%)
2-Naphthalenethiol	99%

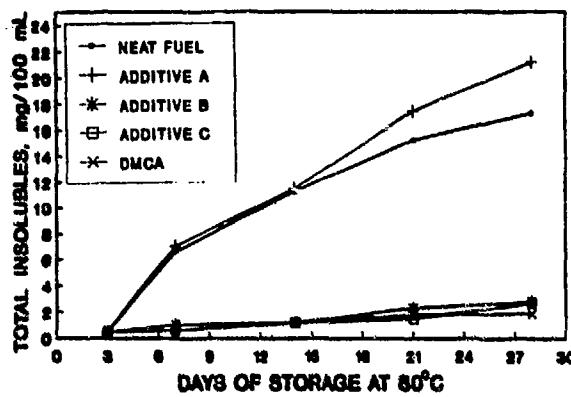
stubborn adherents. The TAM solvent was removed, and the adherent insolubles were determined, using the air-jet method outlined in ASTM Method D 381. Total insolubles were calculated as the sum of filterable and adherent insolubles, and reported as mg/100 mL. Note: all reported total insolubles values are the average of three samples, unless otherwise indicated.

F. Sediment Samples

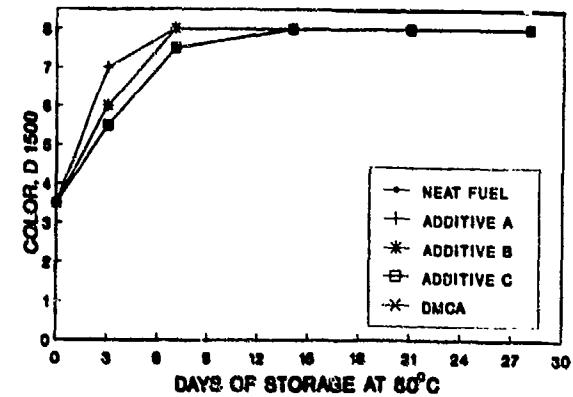
To obtain filterable insolubles samples for analysis, aged fuel samples were filtered through PTFE filters of 1.0- μ m pore size. The filter was then washed several times with filtered isoctane. The particulates were removed from the filter by simply inverting the filter over the sample container and tapping it with a spatula. To obtain adherent insolubles samples, the aging container was rinsed with filtered isoctane to remove the last traces of the fuel. The container was then rinsed with TAM to remove the adherents. The TAM rinsings were collected, and the TAM was evaporated by blowing argon into the container while it was warmed slightly.

III. RESULTS AND DISCUSSION

Figs. 1 through 3 are total insolubles and fuel color data for the aging of the LCO fuel, the Cat 1-H fuel, and a 50/50 blend of the two, respectively. In Fig. 1, note that the dispersant additive, Additive A, had essentially no effect on the formation of insolubles as compared to the neat fuel. The three stabilizer additives, Additives B, C, and DMCA, were all equally effective in reducing the formation of insolubles in the fuel. This close relationship is expected since all three have the same stabilizer component. Note also in Fig. 1 that the fuel color for all samples darkened quickly. All the samples had a color of >8.0 (the maximum color for D 1500) by day 14, regardless of additive treatment. This coloring is significant in that it shows that although a fuel is dark in color, it is not necessarily highly contaminated. In Fig. 2, the pattern of insolubles formation and additive response was quite different from that for the LCO. The results show much less difference between any of the samples, i.e., essentially no noticeable improvement with any of the additives over the untreated fuel. The results for the 50/50 blend, Fig. 3, show a pattern of insolubles formation and additive response that very closely resembles that of the LCO. The primary difference between the blend and the LCO is that in each

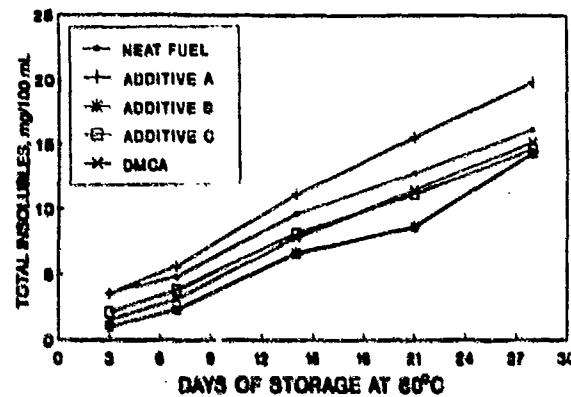


a. Total Insolubles

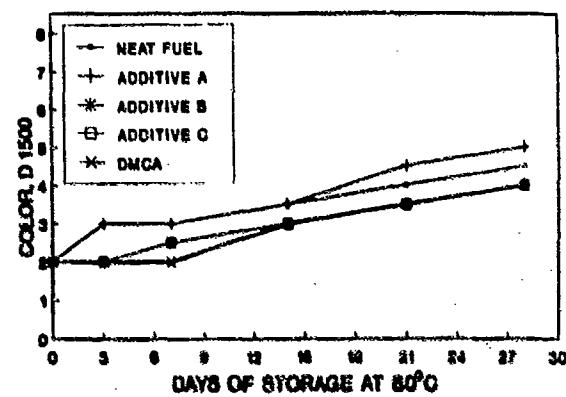


b. Color

Figure 1. Total insolubles and fuel color data for LCO fuel

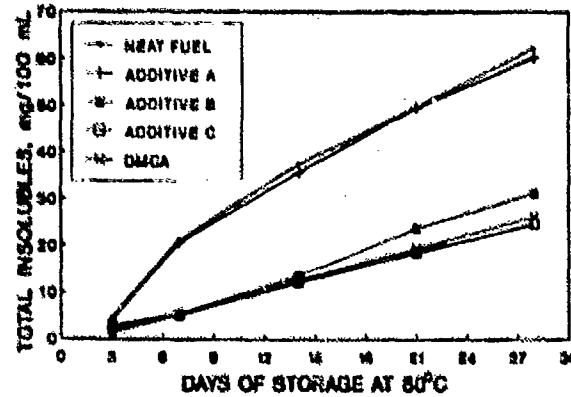


a. Total Insolubles

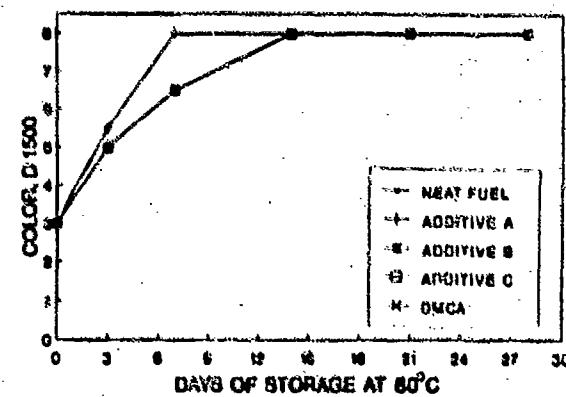


b. Color

Figure 2. Total insolubles and fuel color data for Cat 1-H fuel



a. Total Insolubles



b. Color

Figure 3. Total insolubles and fuel color data for 50/50 blend of LCO/Cat 1-H fuels

case the blend produced more insolubles. It is felt that this difference is caused either by some type of fuel incompatibility, or by the Cat 1-H diluting the solvating power of the LCO, thereby allowing more of the sediment formed in the fuel to drop out of solution.

The relative solvent powers of the three fuels were estimated by determining their Kauri-Butanol (KB) values. The KB test (ASTM D 1133) is used to determine the relative solvent power of hydrocarbon solvents used in paint and lacquer formulations. The KB values of the three test fuels, along with those of some common solvents, are given in TABLE 4. Note that the blend does indeed have a lower KB value than does the LCO.

Since the components of the acidic fraction of the fuel are thought to play the greatest role in the formation of fuel sediment, each of the fuels was next extracted with 1N NaOH to recover the acidic fraction. Reconstitution of each of the acidic fractions, followed by extraction with methylene chloride, produced two brown, highly viscous liquids. The Cat 1-H fuel contained approximately 0.04 wt% of acidic components, while the LCO contained approximately 0.07 wt%. Each fuel sample was submitted for IR analysis. The IR spectra for each are presented in Figs. 4 and 5. Overall, the two spectra are quite similar, with the exception of the slightly larger peak at $\approx 1600 \text{ cm}^{-1}$ in the LCO spectrum. Hazlett, et al.⁽⁹⁾ assigned this peak to aromatic C=C absorptions with intensity enhancement due to ring-oxygen substituents. The peak at $\approx 3400 \text{ cm}^{-1}$ is consistent with the presence of phenolic compounds.

Since some type of an acid-base reaction is often proposed as one of the primary mechanisms for sediment formation in LCO-type fuels, an analysis was also conducted to identify the basic components of the LCO fuel. A portion of the LCO fuel was extracted

TABLE 4. Kauri-Butanol Values

Specimen	Value
Toluene/Acetone/Methanol	>200
Tetrahydrofuran	>200
Benzene	113.3(115)*
Methylnaphthalene	105.0
Toluene	104.2(105)
LCO	92.1
Methylene Chloride	81.2
MS-2	65.5
50% LCO/50% Cat 1-H	47.4
MS-1	35.0
Cat 1-H	32.0
Hexane	27.8(31)
Heptane	27.0(28)
Dodecane	22.1

* Parentheses indicate literature values from ASTM Special Technical Publication 7C.

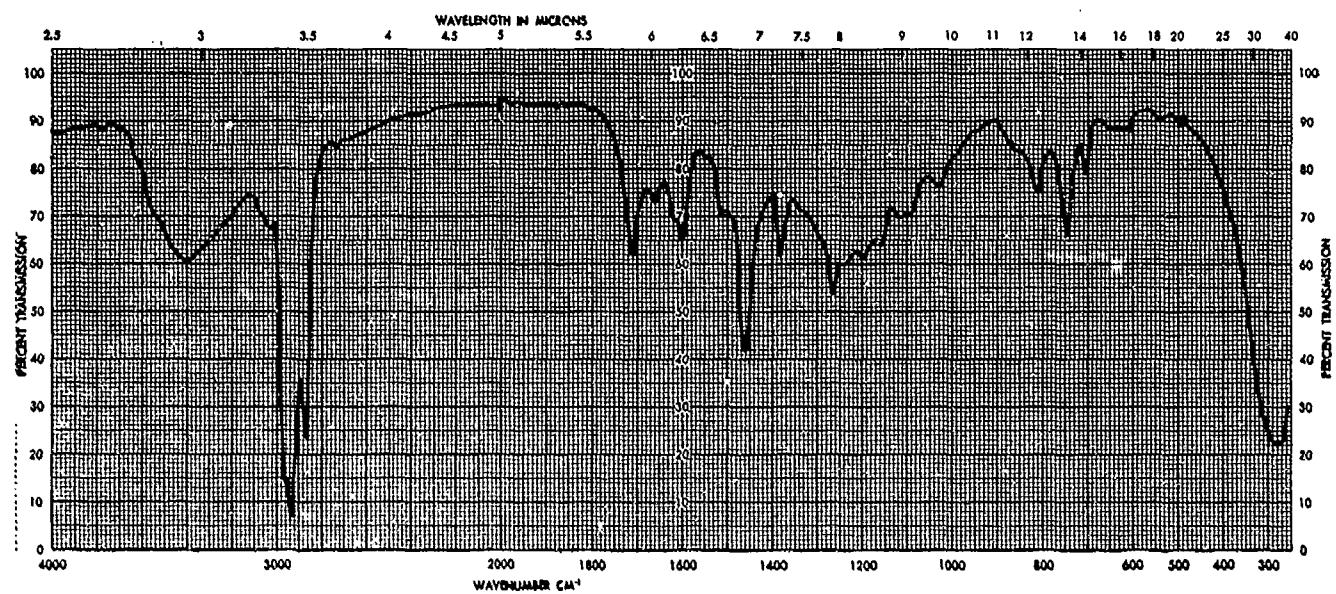


Figure 4. IR spectrum for Cat 1-H caustic extract

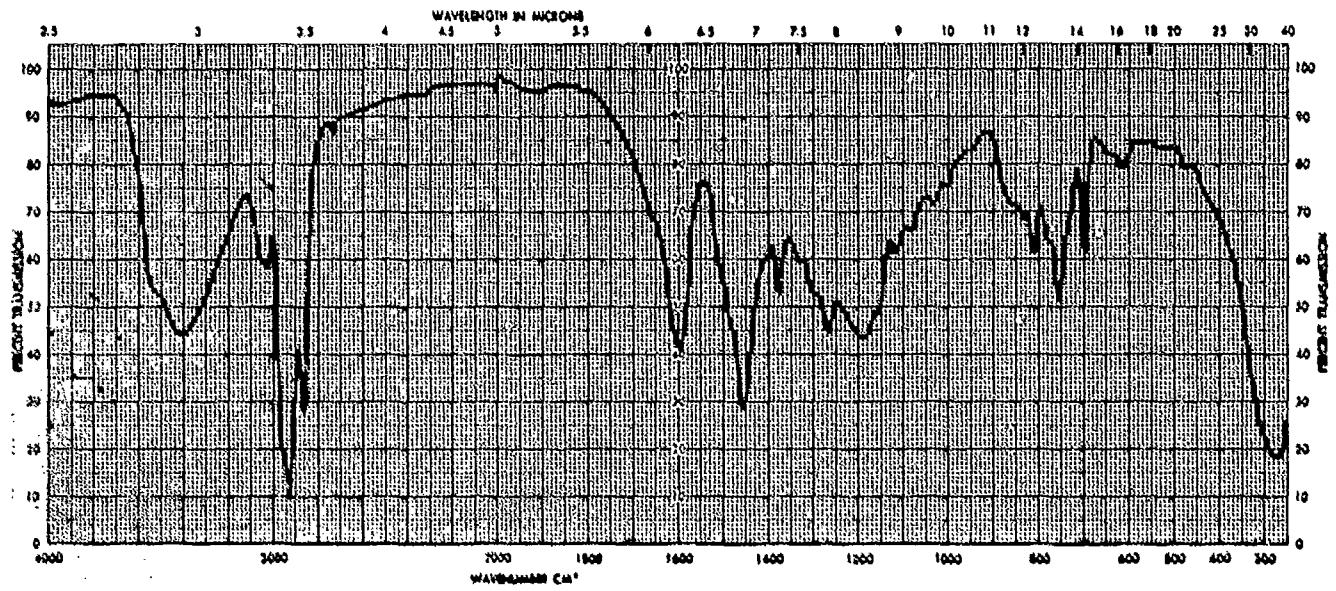


Figure 5. IR spectrum for LCO caustic extract

with 10-percent H_2SO_4 . The extract was analyzed using GC/MS. The chromatogram is pictured in Fig. 6, along with peak assignments. The majority of the compounds isolated were substituted quinolines and isoquinolines.

Peak Assignments

- 1 - C₆ hydrocarbon
- 2 - C₇ hydrocarbon
- 3 - mono-substituted quinolines and isoquinolines
- 4 - di-substituted quinolines and isoquinolines
- 5 - tri-substituted quinolines and isoquinolines
- 6 - contaminant

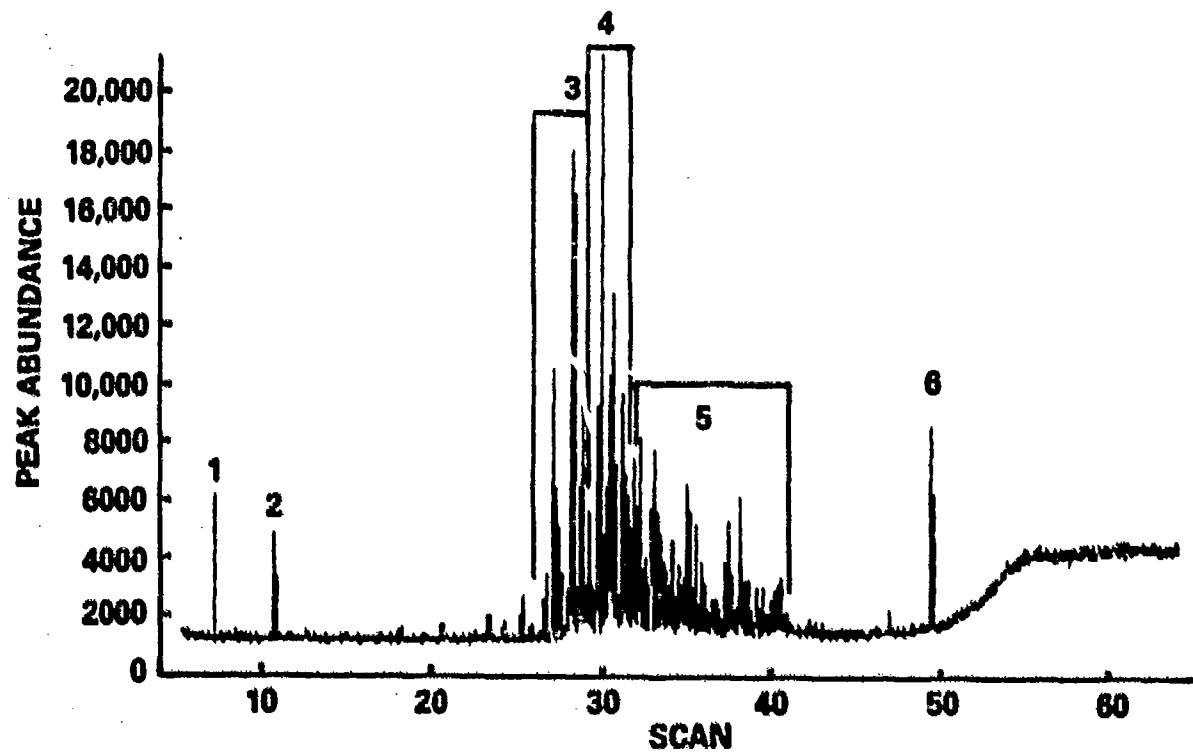


Figure 6. Gas chromatogram of H_2SO_4 extract from LCO fuel

From this point forward, all work was done with the LCO only. It was felt that: 1) The acidic component of the fuel was of primary concern, and the LCO contained a higher percentage of acidic components. 2) The LCO tended to form more insolubles during aging, thus providing more sample for analysis. 3) As described above, the Cat 1-H had little variation in additive response, with the additives tested. 4) Finished diesel fuels that contain no cracked components were relatively scarce.

Particulate from LCO that had been aged for 3 weeks was analyzed for elemental composition. The results are given in TABLE 5. Ignoring the iron and other categories, and assuming one nitrogen atom per molecule, these results yield an empirical formula of $C_{21}H_{19.56}NO_{2.02}S_{0.14}$ for an average sediment molecule.

Fig. 7 is the thermal-gravimetric analysis (TGA) plot for the 3-week 800°C-aged particulates. The TGA shows that only about 55 percent of the particulates are volatile below 1000°C. These results were confirmed by pyrolysis gas chromatography/mass spectroscopy (pyGC/MS).

TABLE 5. Elemental Analysis of LCO Particulates

Element	Amount Detected wt%
C	72.54
H	5.63
N	4.03
O	9.31 (by difference)
S	1.32
Fe	5.84
Others*	1.33

* Mn, Cr, Al, Si, P, Ca, & Cl

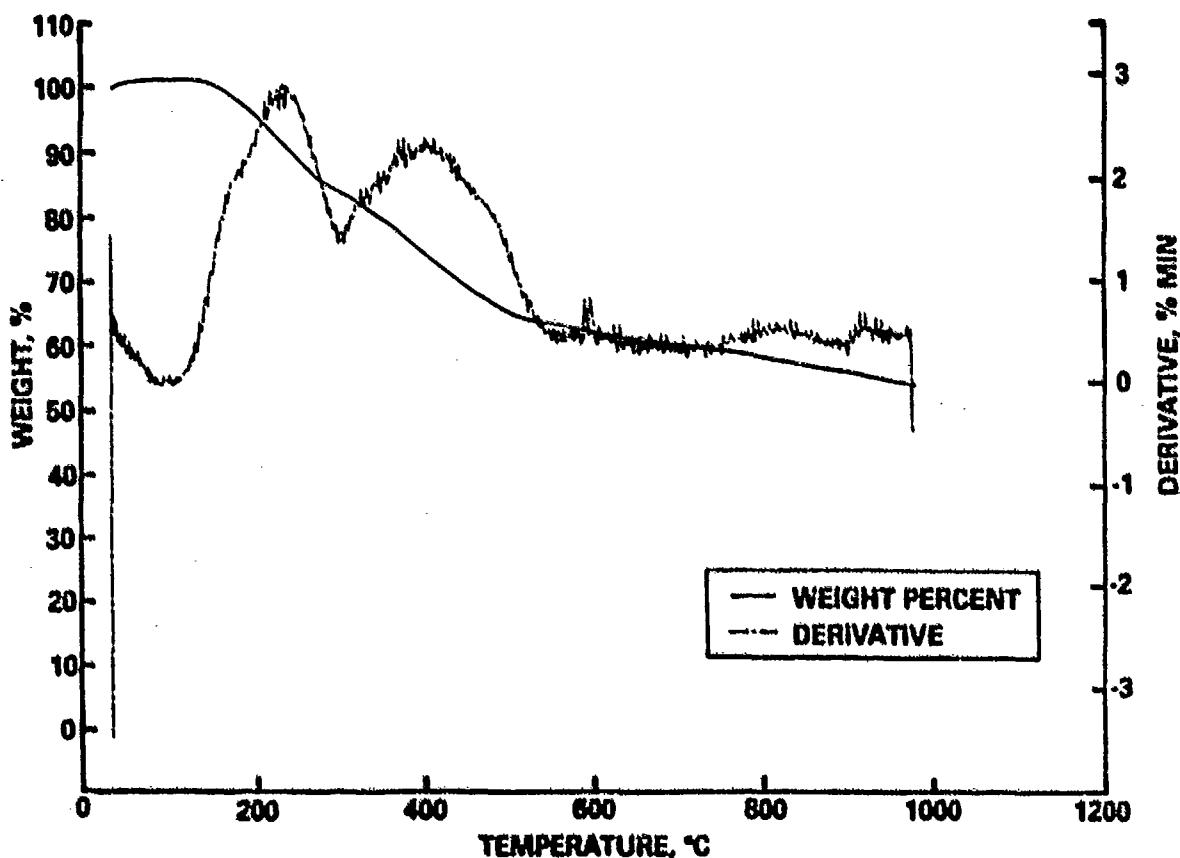


Figure 7. Thermal gravimetric analysis plot for LCO particulates

PyGC/MS analysis was conducted first at 600°C. Fig. 8 is the chromatogram for this analysis, and peak assignments are found in TABLE 6. The results indicate that the

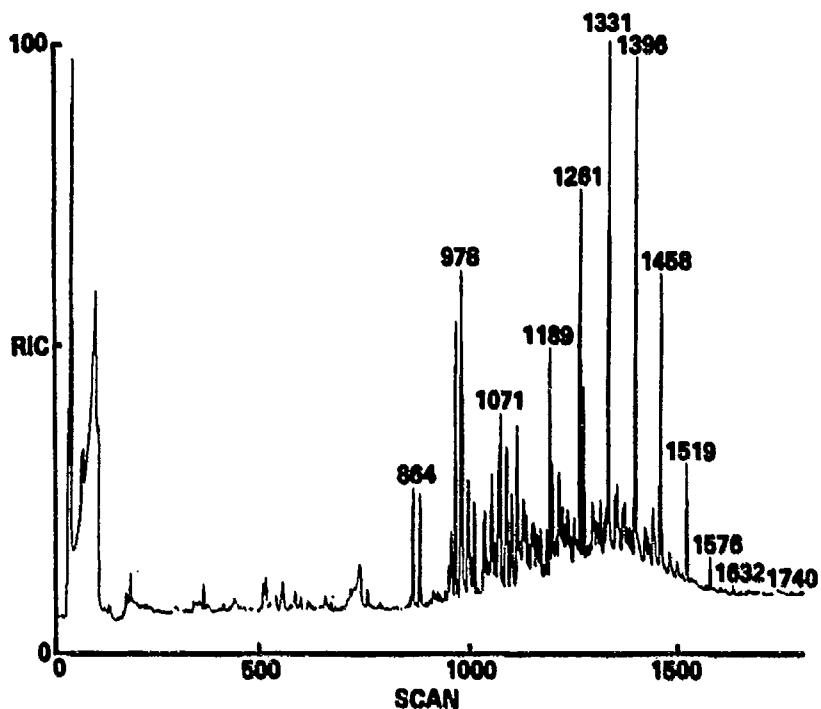


Figure 8. PyGC/MS chromatogram at 600°C for LCO particulates

TABLE 6. Peak Assignments for pyGC/MS of LCO Particulates at 600°C (See Fig. 8)

Scan Number	Assignment
864	1H-Indene, 1-Ethylidene
880	1H-Indene, 1-Ethylidene
964	Dimethyl Naphthalene
978	Dimethyl Naphthalene
994	Dimethyl Naphthalene
1008	Ethyl Naphthalene
1048	t-Butyl Naphthalene
1067	Trimethyl Naphthalene
1071	Trimethyl Naphthalene
1085	Trimethyl Naphthalene
1098	Trimethyl Naphthalene
1112	5-Ethyl, 5-Methyl Decane
1189	Heptadecane
1261	Column Bleed
1269	Phenanthrene
1331	Nonadecane
1396	Column Bleed
1458	Docosane
1519	Docosane

majority of the compounds that volatilize at 600°C are indenes and substituted naphthalenes, both of which were present in the unaged fuel. It is assumed that these compounds were trapped in the matrix of the particulates, since they were not washed away during the sample workup, and were only released upon heating. PyGC/MS was next conducted at 1000°C. To eliminate interferences from the trapped fuel constituents, the pyrolysis probe was left in the interface for 30 minutes at a temperature of 225°C prior to pyrolysis. Fig. 9 and TABLE 7 are the pyGC/MS chromatogram and the peak assignments for this analysis, respectively. As can be seen from this analysis, the particulates are essentially

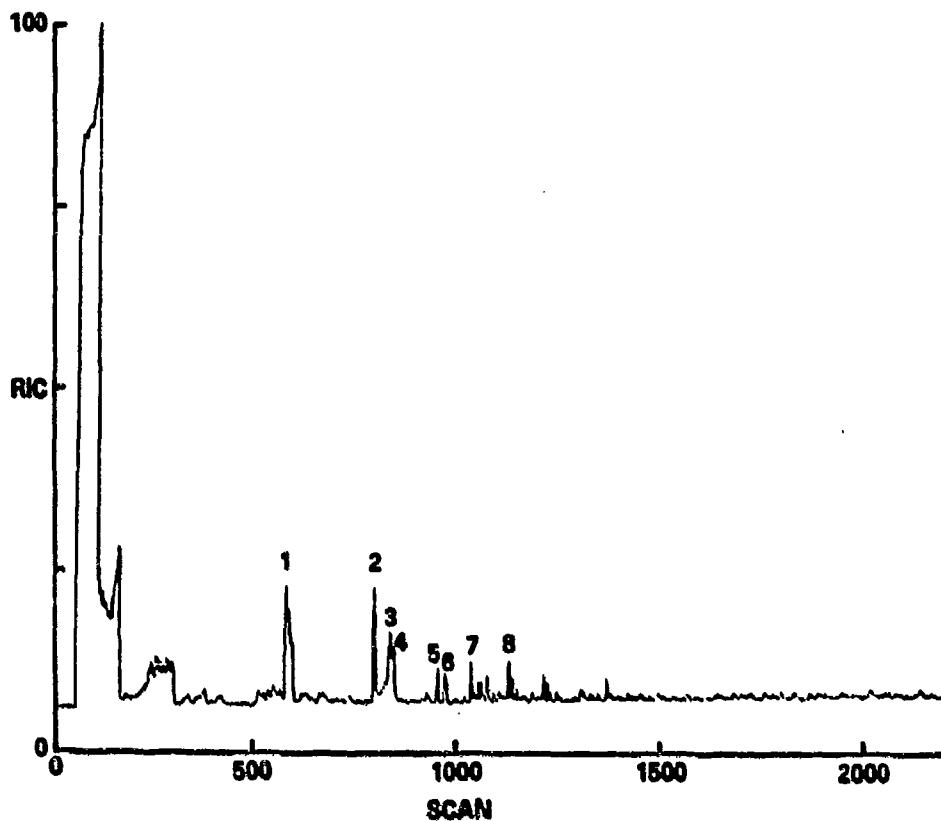


Figure 9. PyGC/MS chromatogram at 1000°C for LCO particulates

TABLE 7. Peak Assignments for pyGC/MS of LCO Particulates at 1000°C (see Fig. 9)

Peak No.	Assignment
1	Column Bleed
2	Column Bleed
3	Naphthalene
4	Benzoic Acid
5	1H-Indene, 1-Ethylidene
6	1H-Indene, 1-Ethylidene
7	1,1'-Biphenyl
8	3-Methyl 1,1'-Biphenyl

nonvolatile at 1000°C; however, the 30-minute preheating step does remove the majority of the trapped fuel components. The chromatogram for pyGC/MS at 1400°C is given in Fig. 10. A total of 65 peaks were integrated and identified. Aside from indenes, naphthalenes, saturated hydrocarbons and olefins, compound classes that were found in relatively large amounts include: indoles, carbazoles, phenols, thiophenes, and fluorenes. Found in lesser amounts were amines and pyrans. It is

not known, however, how many of the compounds identified in the 1400°C pyGC/MS may have been formed by the pyrolysis.

In order to further study the nature of the particulates, approximately 100 mg of the particulates were recovered from LCO that had been aged at 80°C for 9 weeks. These particulates were subjected to the solvent extraction scheme shown in Fig. 11. The

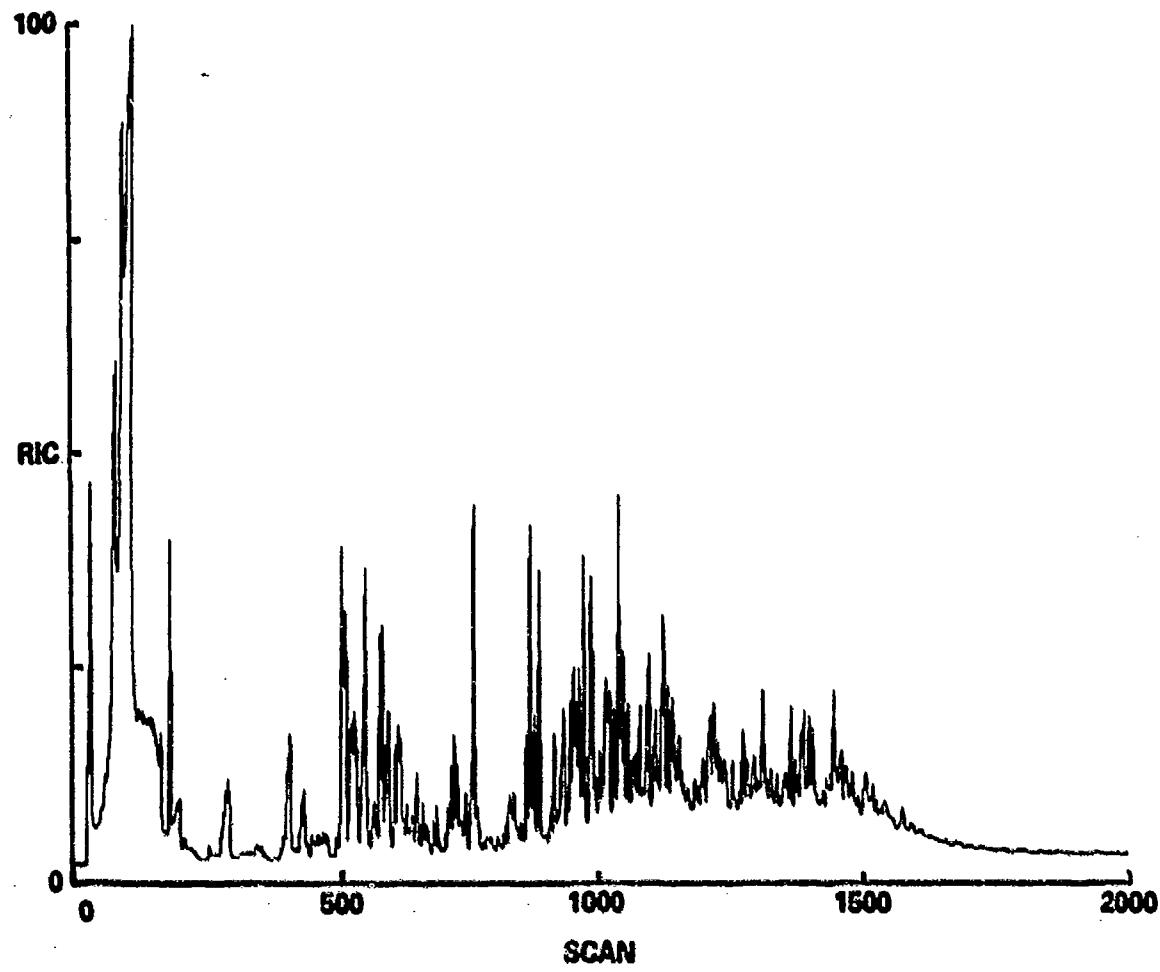
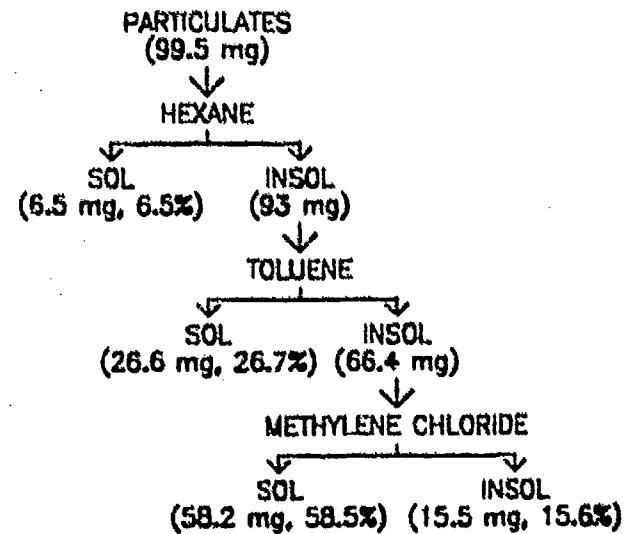


Figure 10. PyGC/MS chromatogram at 1400°C for LCO particulates



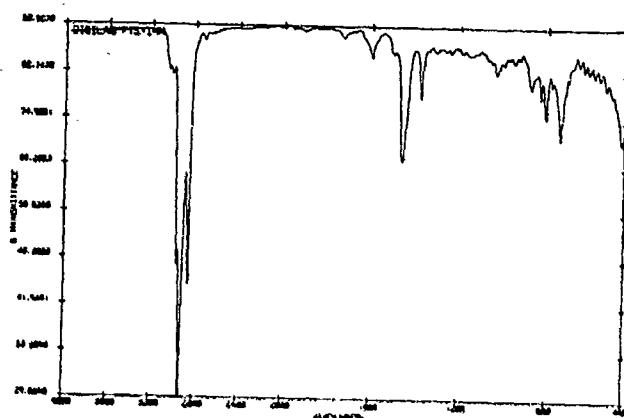
APPROXIMATELY 1% LOSS

Figure 11. Solvent extraction scheme and results

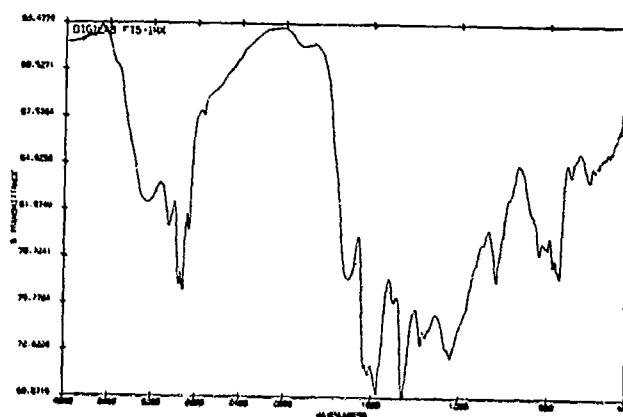
amount of material recovered at each step is also given in the figure. Each of these fractions was submitted to Fourier transform infrared (FTIR) analysis to determine differences. Fig. 12 is a compilation of the FTIR spectra for each of the fractions. Note that, with the exception of the hexane-soluble fraction (trapped, unaged, fuel components), there is very little significant difference between the spectra. Perhaps the primary difference between these fractions is in the average molecular weight of the sediment molecules in each. This observation is confirmed somewhat by the field ionization mass spectrum (FIMS) of the particulates (in Fig. 13), which shows three distinct groupings of peaks. This FIMS spectrum is very similar to spectra obtained by Malhotra and St. John⁽⁷⁾, who reported that the periodicity of the peaks is indicative of dimeric, trimeric, etc., coupling products. Attempts to recombine the fractions, by mixing, to produce sediment similar to the original in composition and texture, were unsuccessful. Additional FIMS spectra are presented in the appendix for comparison. These spectra demonstrate that there are differences between insolubles from different sources. As can be seen, the average molecular weight of the insolubles seems to increase as the fuel gets heavier.

Based on the data given previously, as well as other reported findings^(6,9,13), a model system was developed. The components of the model system, labeled MS-1, are given in TABLE 8. They are divided into those components that represent the fuel, or solvent matrix, and those thought to be the sediment-forming compounds. Samples of MS-1 and MS-1 plus each of the four additives were aged at 80°C for periods up to 28 days. The total insolubles and color data are given in Fig. 14. Note that there was little change in the color of the samples and no consistent pattern to sediment formation in any of the samples. A white precipitate had been noticed in several of the samples, especially after the samples had cooled to room temperature. This precipitate seemed to constitute a large portion of the filterable insolubles obtained from each sample. Analysis of the precipitate showed that it was p-phenylphenol. During the preparation of the MS-1 samples, difficulty was experienced in getting the p-phenylphenol to fully dissolve. Also GC/MS analysis of the sediments formed by MS-1 showed only the starting reagents. For these reasons, it was felt that the MS-1 was not an accurate model of an LCO fuel.

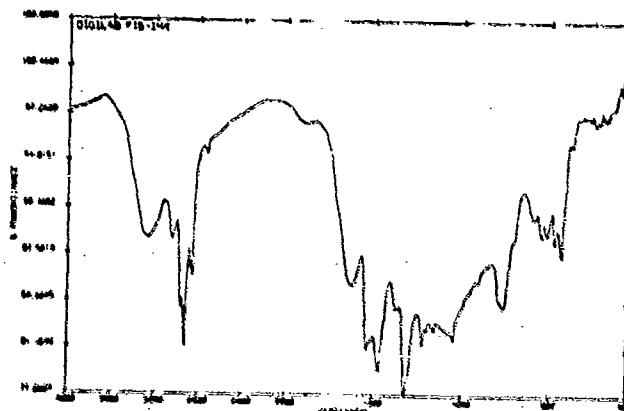
Further review of laboratory data and the literature revealed that MS-1 should include a sulfur-containing compound, probably a thiol or a sulfonic acid. The findings of Hazlett, et al.⁽⁹⁾ indicated that the acid probably had the greatest influence on sediment



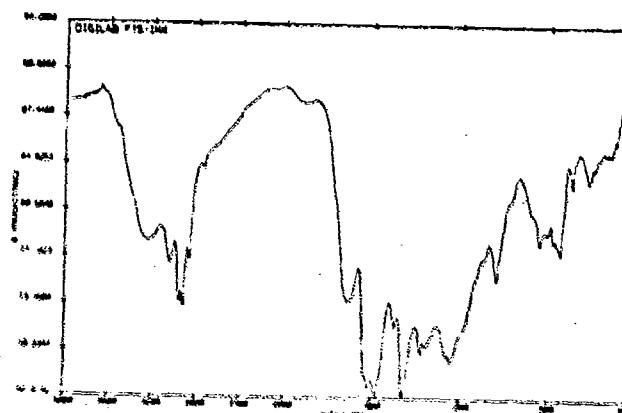
a. Hexane Soluble



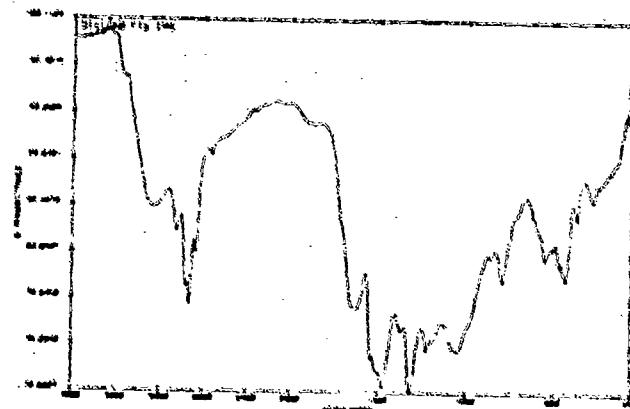
b. Hexane Insoluble



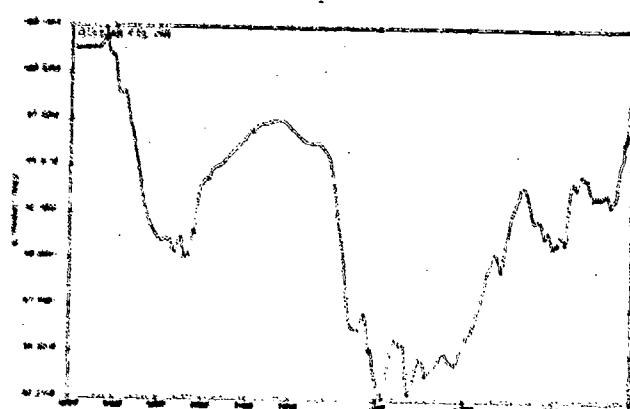
c. Toluene Soluble



d. Toluene Insoluble



e. Methylene Chloride Soluble



f. Methylene Chloride Insoluble

Figure 12. FTIR spectra for solvent-extracted LCO particulates

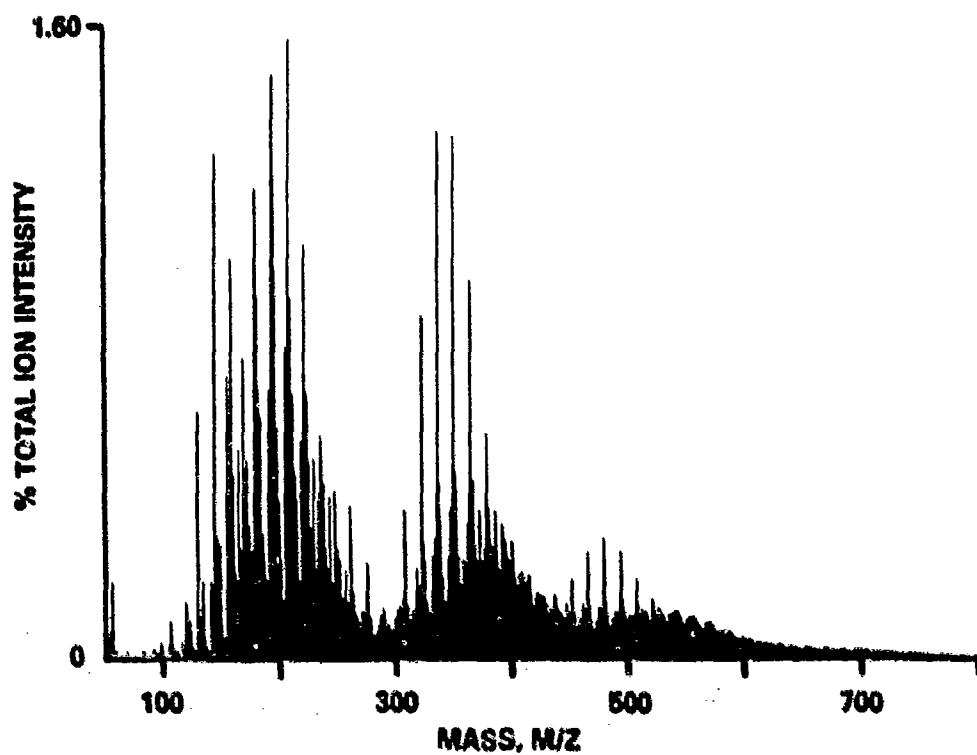


Figure 13. FIMS spectrum for LCO particulates

TABLE 3. Composition of MS-1

Solvent Matrix

Component	vol%
n-Dodecane	62.5
n-Butylbenzene	32.5
MethylNaphthalene	2.0
1-Octadecene	3.0

Reactants

Component	mmol/L
Indole	27.5
Benzoic Acid	27.5
p-Phenylphenol	27.5
Quinoline	52.5

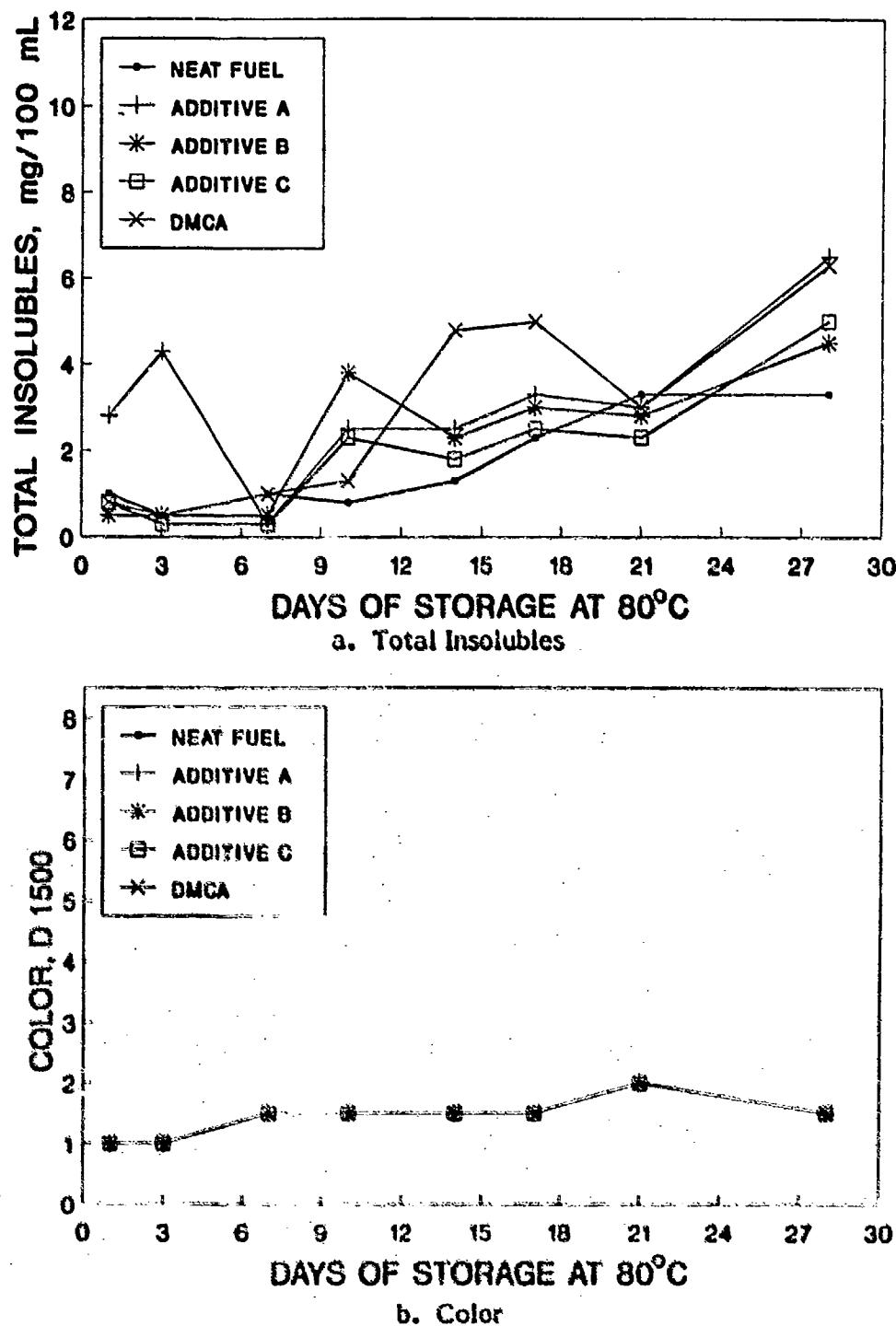


Figure 14. Total insolubles and color data for aging of MS-1 at 80°C

formation. The model system was reformulated to produce MS-2. The composition of MS-2 is given in TABLE 9. There are several differences between MS-1 and MS-2. The solvent matrix was changed to make its concentration of saturates, olefins, and aromatics more closely resemble that of the LCO (see TABLE 1). The concentrations of

TABLE 9. Composition of MS-2

Solvent Matrix

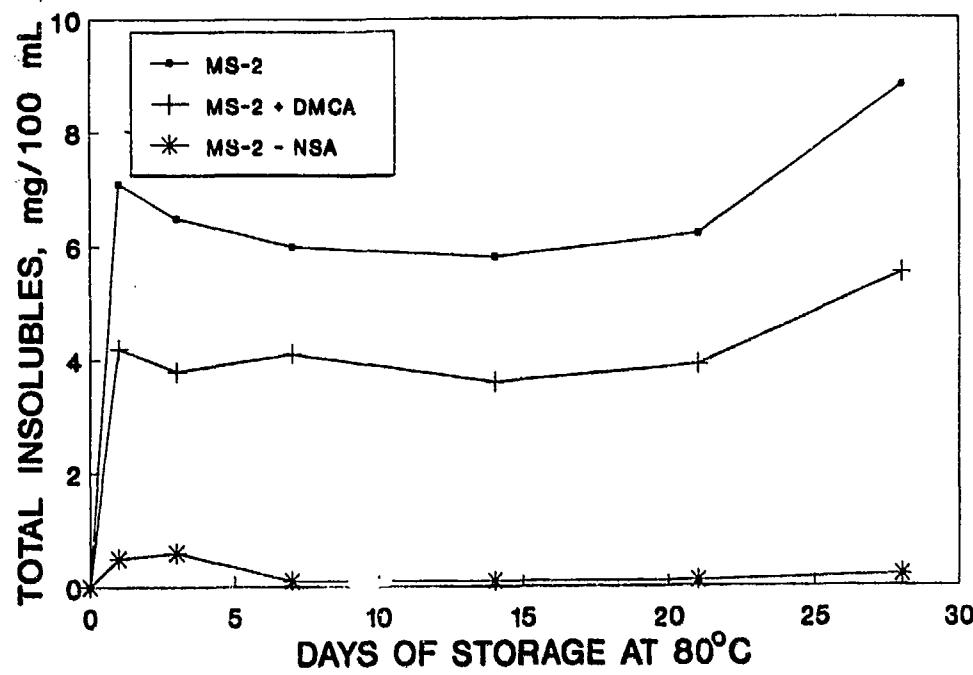
Component	vol%
n-Dodecane	27.5
n-Butylbenzene	60.0
Methylnaphthalene	5.0
1-Octadecene	2.5
1-Butanol	5.0

Reactants

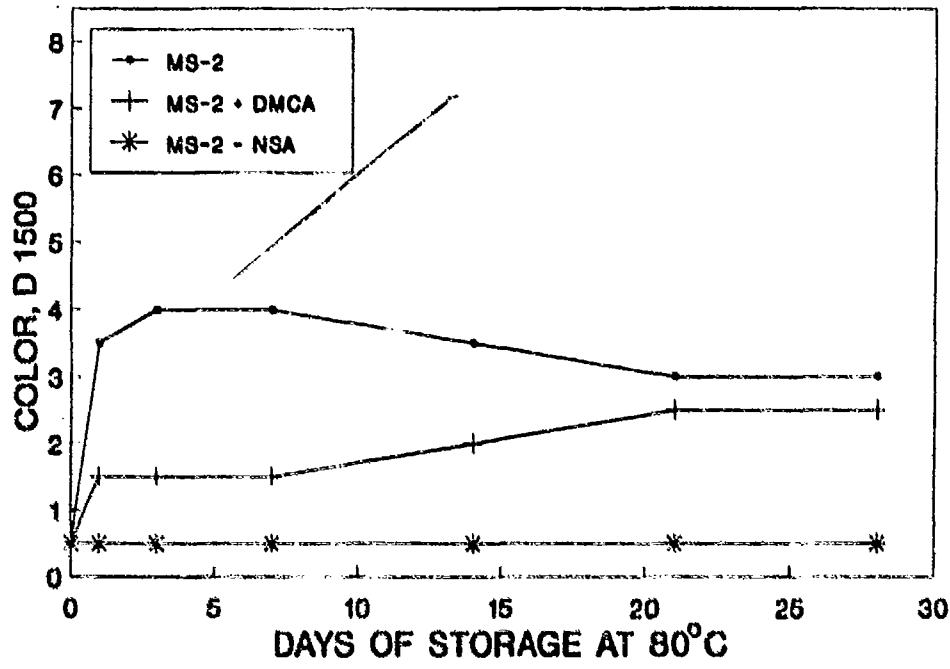
Component	mmol/L
Methyl Indole	0.5
Benzoic Acid	0.25
p-Phenylphenol	0.5
Quinoline	1.0
Naphthalene Sulfonic Acid	0.5

each of the sediment-forming components were lowered. The other significant change was the addition of naphthalene sulfonic acid (NSA). The 1-butanol was added to the solvent matrix to facilitate addition of the NSA. When preparing the MS-2 samples for aging, the methylindole was the last component added. It was noted that addition of the indole to samples with NSA in them was followed almost immediately by the appearance of a light red color in the liquid. No such color change occurred in the MS-2 without NSA.

The total insolubles and color data for the aging of MS-2, MS-2 plus DMCA, and MS-2 without NSA at 80°C are given in Fig. 15. These data show an interesting pattern, different from that of the LCO. It appears from the data that essentially all the sediment formation occurred within the first day of aging; only after 21 days of storage was any additional sediment formed. The presence of DMCA reduced the amount of total insolubles formed, but the same pattern of insolubles formation was followed. The MS-2 without NSA formed no insolubles. This pattern indicates that a necessary component was consumed during the first day. Presumably the increase after 21 days of storage is due to either a different reaction mechanism with a longer induction period or the formation of additional reactant in the system.



a. Total Insolubles



b. Color

Figure 15. Total insolubles and color data for aging of MS-2 at 80°C

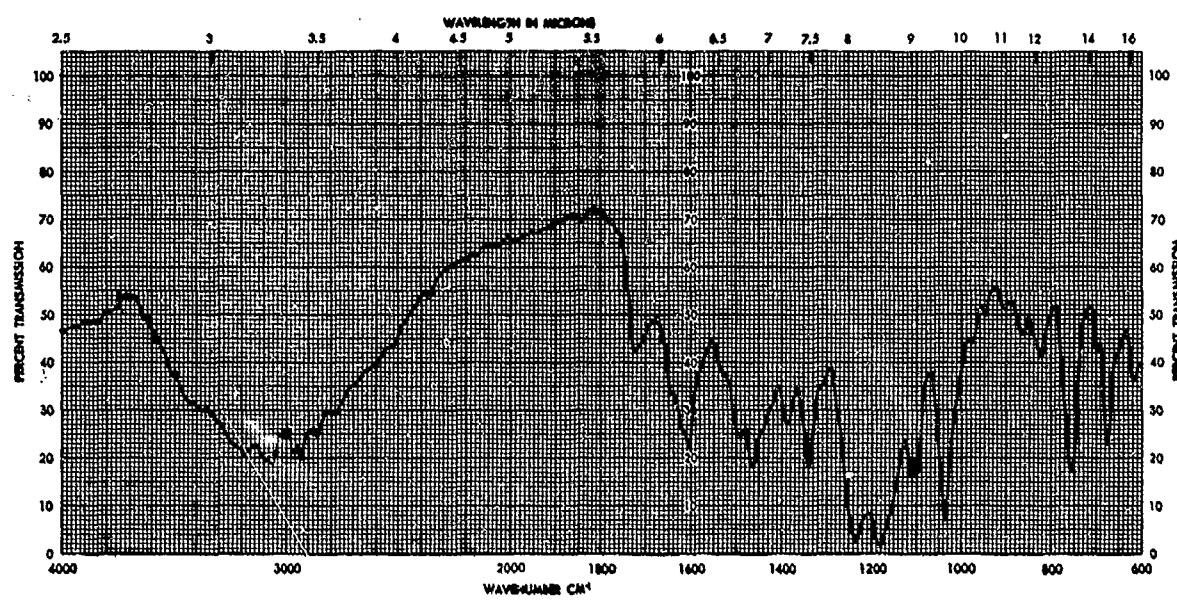
Most likely, the DMCA is reacting with the NSA to neutralize the acid and reduce the sediment-forming capacity of the NSA. If one assumes that the NSA and the DMCA are reacting on a 1:1 basis as reported elsewhere⁽⁹⁾, then a reduction of approximately 48 percent in the amount of total insolubles formed would be expected. The data indicate a

consistent reduction of between 38 and 43 percent with the presence of DMCA. This trend is by no means conclusive evidence of the mechanism, but it does strongly indicate that this type of reaction is occurring.

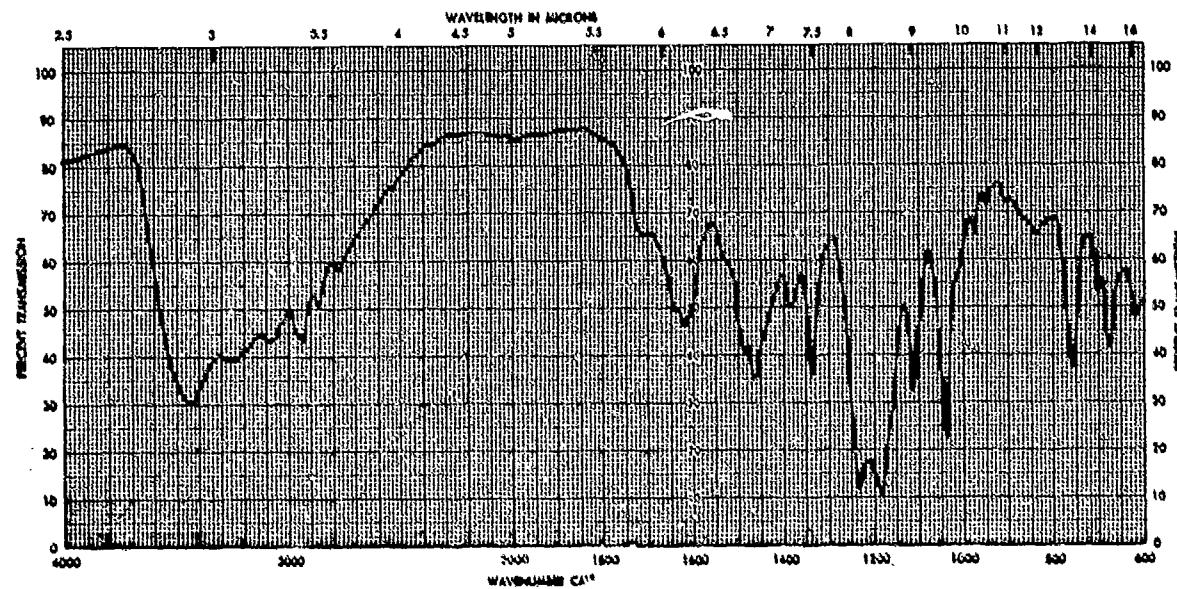
Hazlett, et al.(9), reported that three different carboxylic acids act as sediment promoters but are not incorporated into the sediment. They also reported that dodecylbenzenesulfonic acid (DBSA) promotes sediment formation and, in contrast, may be incorporated into the sediment. BFLRF found that the NSA is indeed incorporated into the sediment. Analysis of the sediment by X-ray fluorescence (XRF) showed varying amounts of sulfur ranging from 0.6 to 3.4 wt%. The IR spectra for the sediment from the aging of MS-2 and MS-2 plus DMCA are given in Fig. 16. The peaks at 675, 1040, and 1185 cm^{-1} are consistent with the presence of NSA in the sediments and are assigned to S=O stretching. In addition, the peak at $\approx 3440\text{ cm}^{-1}$ in the spectrum for MS-2 plus DMCA is consistent with the presence of the amine in the sediment. This finding is in contrast to earlier work(9), which indicated that the DMCA was not incorporated into the sediment. It is likely that the basic DMCA is reacting with the NSA. It is also important to note that the IR spectrum for the MS-2 particulates is very similar to the IR spectrum for the LCO particulates (see Fig. 12).

Another storage test was conducted to determine the effect of NSA concentration on sediment formation. Samples of MS-2, with NSA at concentrations of 0, 0.5, 1.0, 2.0, and 4.0 mmol/L, were stored at 80°C for 14 days. The results are shown in Fig. 17. BFLRF results agree with those of Hazlett, et al.(9), in that there is a square root relationship between the concentration of the NSA and the amount of total insolubles formed. These results also indicate that the NSA is the limiting reagent in the storage tests presented in Fig. 15.

Since thiols are also known to promote sediment formation, a test was conducted to determine the effect that a thiol would have. Samples of MS-2 with and without NSA and DMCA, but all with naphthalenethiol (NT), were aged at 80°C for periods up to 28 days. The total insolubles and color data are presented in Fig. 18. As before, the samples containing NSA formed the most insolubles; the presence of DMCA reduced the amount formed. Unlike the data in Fig. 15, the samples with NSA had a fairly steady increase in insolubles formation throughout the aging. This steady increase is most likely due to the presence of the thiol in the mixture. The sample with NT but no NSA required



a. MS-2



b. MS-2 + DMCA

Figure 16. IR spectra for particulates from 800°C aging

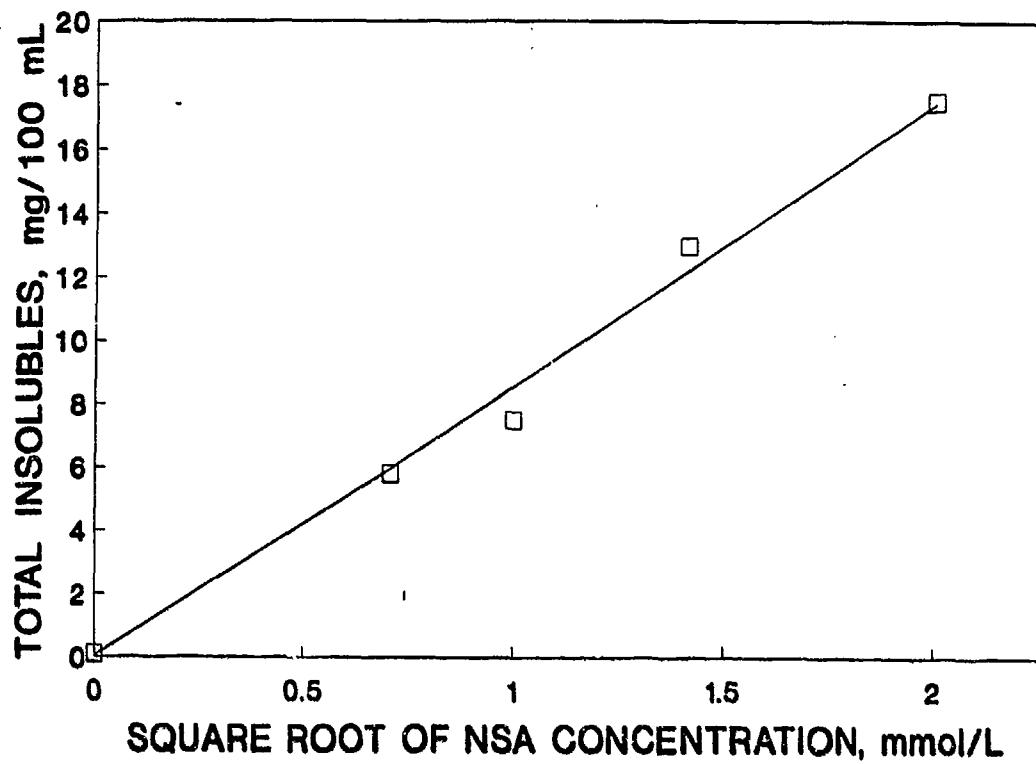


Figure 17. Effect of NSA concentration on total insolubles formation in MS-2

an induction period before much insolubles were formed. Presumably, this induction period is related to the oxidation of the NT to NSA. The sample with DMCA and NT but no NSA formed only a small amount of insolubles throughout the test. The DMCA is essentially neutralizing the NSA as it is formed. The only sample that had no color change during the entire test (a change from 1.0 to 0.5 is within the repeatability of the D 1500 color test) was the sample with DMCA and NT but no NSA. The other samples all had an increase in color and all reached approximately the same color by the end of the aging, 3.0 ± 0.5 . These data support the data presented in Fig. 15, which indicates that it is the reaction of NSA with another substance that causes the color formation.

IV. CONCLUSIONS

This work confirms earlier findings that diesel fuel insolubles are formed through various mechanisms, depending upon the composition of the fuel. The importance of certain acidic components of the fuel as sediment promoters and as limiting reagents to sediment formation was demonstrated.

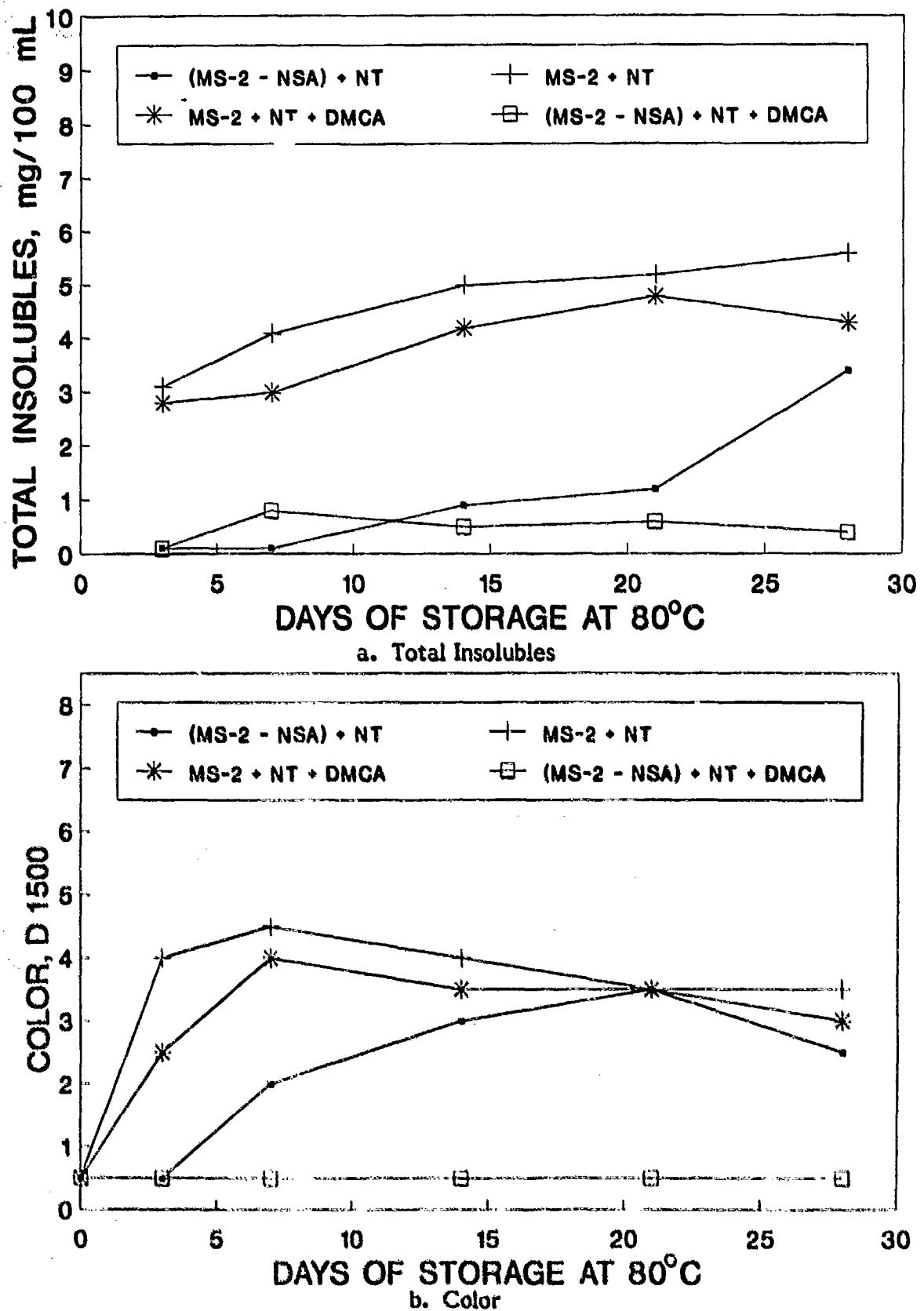


Figure 18. Total insolubles and color data for the aging of MS-2, plus naphthalenethiol, at 80°C

A model system was developed based on the analysis of actual fuels and fuel sediments. This model system produces fuel insolubles that are quite similar to those from actual fuels.

The usefulness of this model system for the study of additive inhibition and insolubles formation mechanisms was shown. The amount of insolubles formed was found to be directly related to the square root of the concentration of naphthalene sulfonic acid (NSA) in the system. Analysis of the sediments formed by the model system showed that the NSA is incorporated into the sediment.

This system is also valuable as a tool for estimating inhibitor additive response. The addition of N,N'-dimethylcyclohexylamine (DMCA) to the system caused a marked decrease in the amount of insolubles formed. The data indicated that the DMCA reduces sediment formation by reacting on an equimolar basis with the NSA to neutralize the acid. Further studies are required to elucidate in greater detail the actual sediment-forming reactions.

The presence of thiols will promote insolubles formation, although not as quickly as will the analogous sulfonic acid. The thiol must first be oxidized to the sulfonic acid.

An increase in the color of a fuel does not necessarily indicate an increase in the formation of insolubles.

The reaction of certain acidic compounds, such as NSA, with nonbasic nitrogen compounds, such as indoles and carbazoles, appears to be one of the methods by which fuel insolubles are formed. The specific mechanism is not yet clear.

V. RECOMMENDATIONS

The following recommendations are made as a result of the work performed in this program.

- The insolubles formed by the aging of MS-2 should be studied in more detail in an effort to identify them. These analyses would also clarify the mechanism by which DMCA reduces sediment formation.

- A matrix study of MS-2 should be conducted to determine what components are required for insolubles formation.
- Basic compounds analogous to DMCA should be evaluated for their ability to inhibit insolubles formation. These compounds could possibly be listed in VV-F-800 as allowable fuel preservative additives.

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APPENDIX
Additional FIMS Spectra

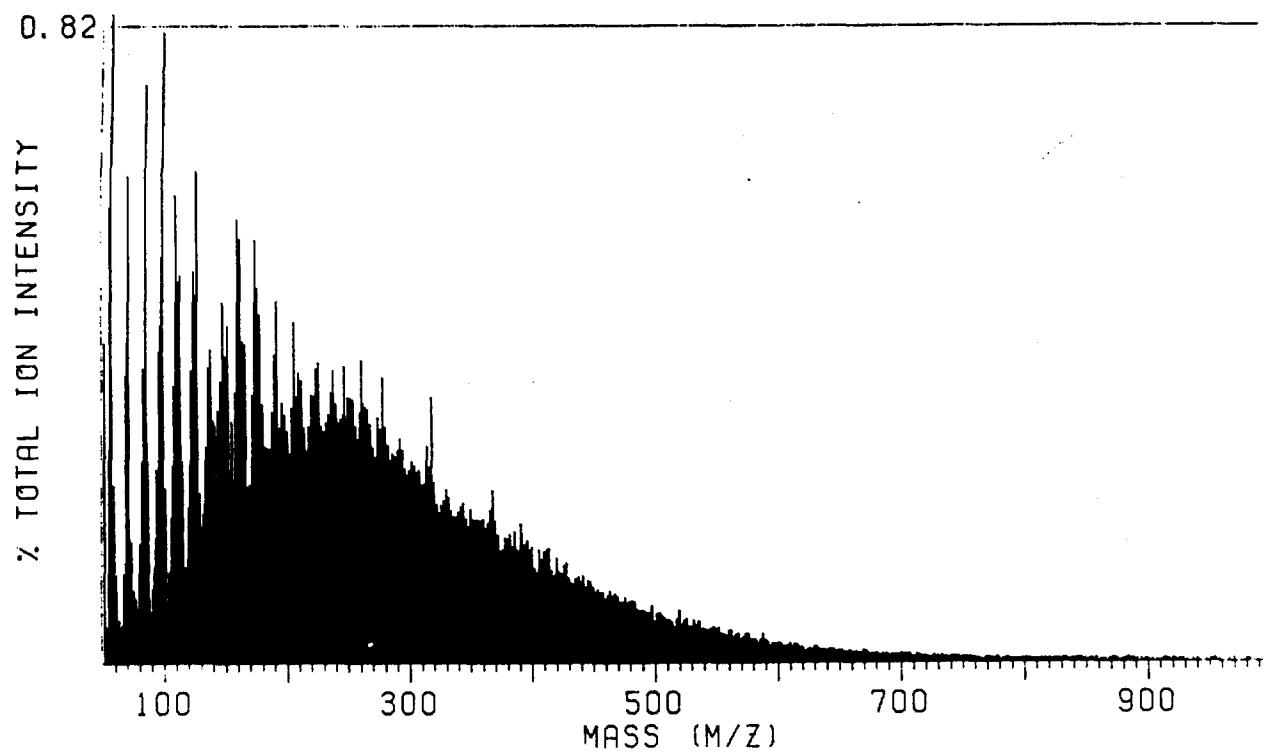


Figure A-1. FIMS spectra for gasoline deposits from ASTM D 873 (mod)

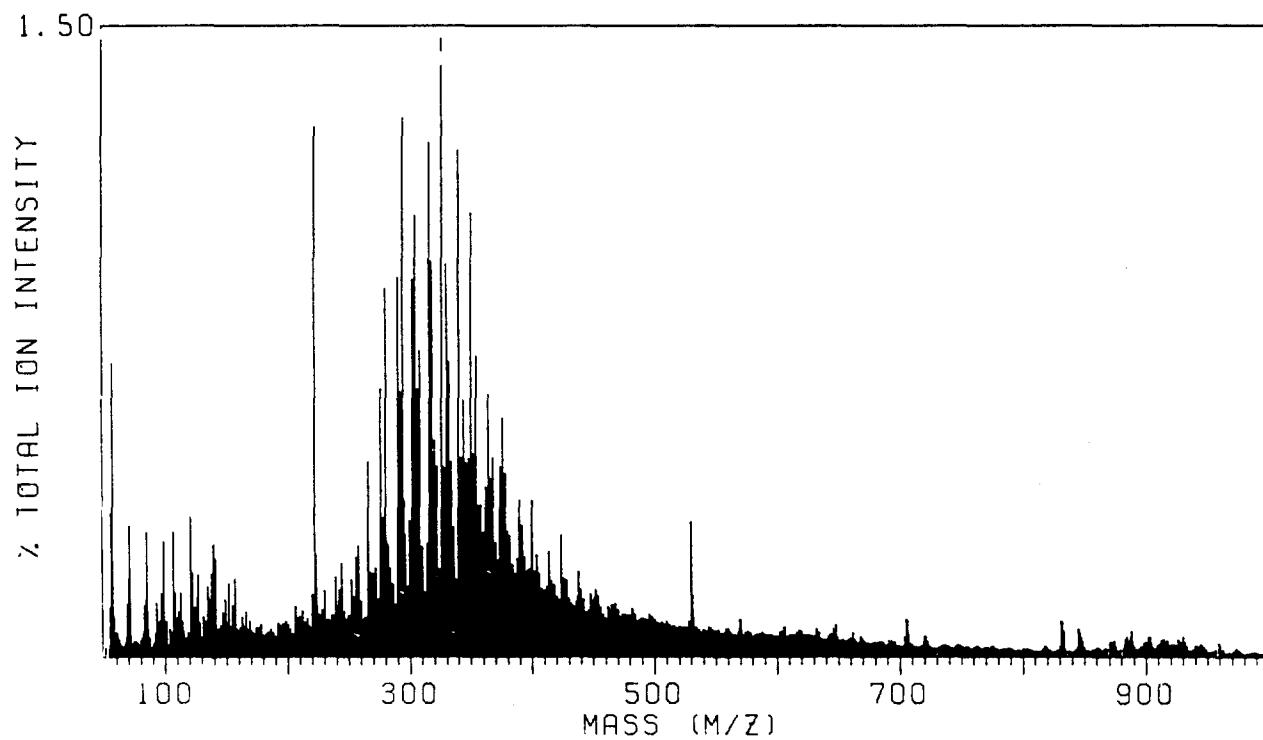


Figure A-2. FIMS spectra of gasoline deposits from induction system deposit test tube

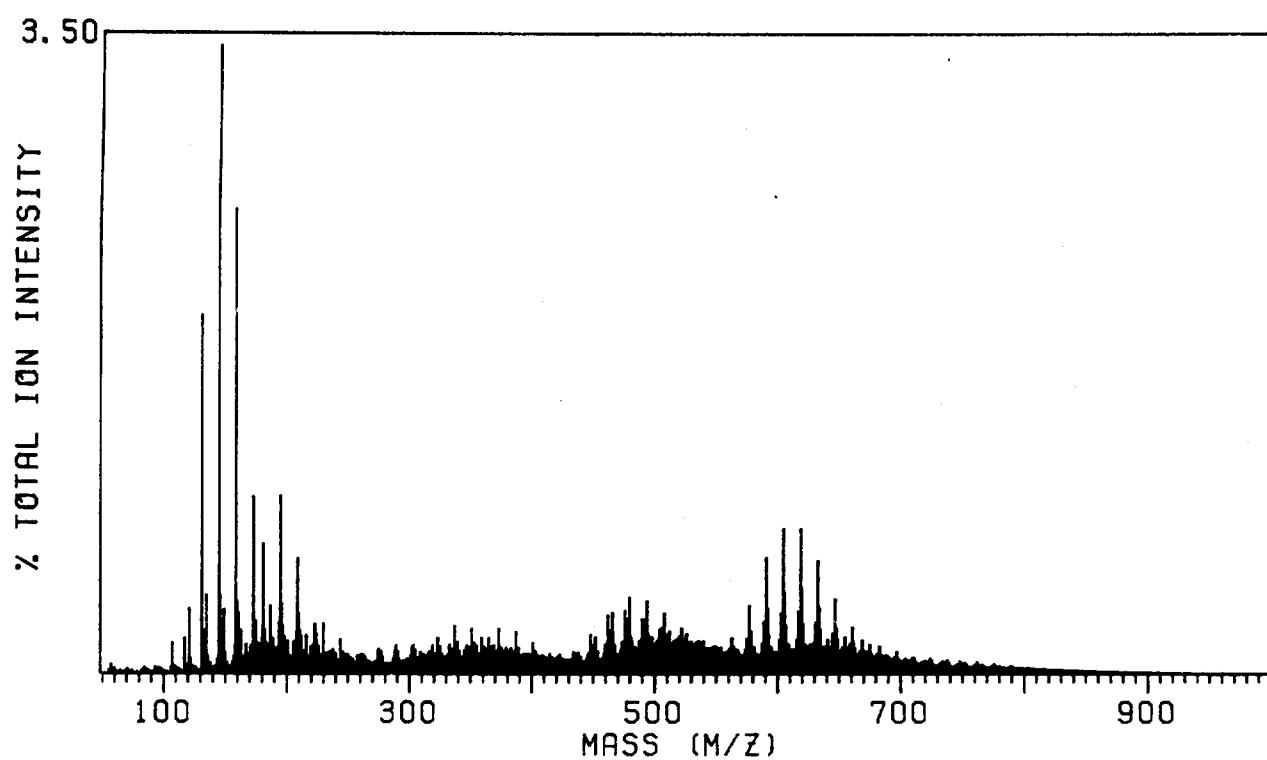


Figure A-3. FIMS spectra of particulates from a Naval distillate fuel

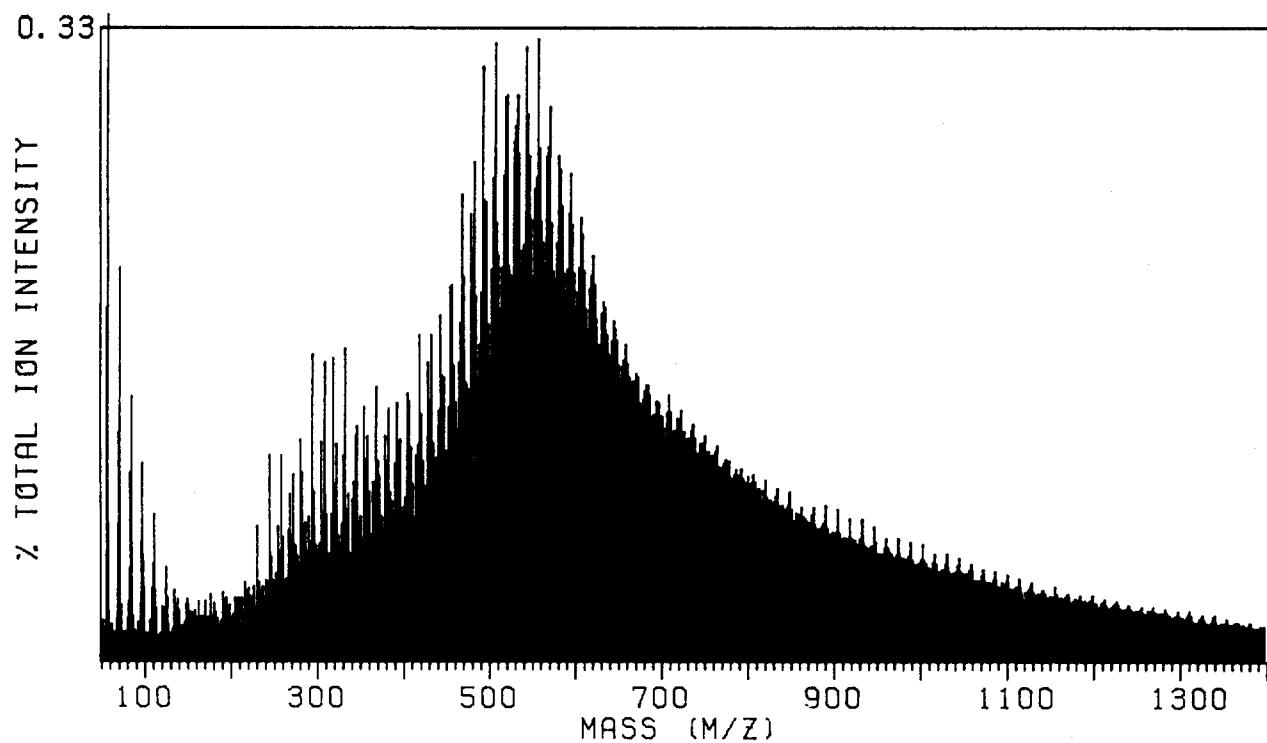


Figure A-4. FIMS spectra of asphaltenes

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CDR US ARMY YUMA PROVING GROUND ATTN: STEYP-MT-TL-M (MR DOEBBLER) YUMA AZ 85364-9103	1	PROJ OFF, AMPHIBIOUS AND WATER CRAFT ATTN: AMCPM-AWC-R 4300 GOODFELLOW BLVD ST LOUIS MO 63120-1798	1
CDR US ARMY RESEARCH OFFICE ATTN: SLCRO-EG (DR MANN) SLCRO-CB P O BOX 12211 RSCH TRIANGLE PARK NC 27709-2211	1	DIR AMC PACKAGING, STORAGE, AND CONTAINERIZATION CTR ATTN: SDSTO-TE-S TOBYHANNA PA 18466-5097	1
CDR US ARMY TANK-AUTOMOTIVE CMD PROGR EXEC OFF COMBAT SUPPORT PM LIGHT TACTICAL VEHICLES ATTN: AMCPM-TVL PM MEDIUM TACTICAL VEHICLES ATTN: AMCPM-TVM PM HEAVY TACTICAL VEHICLES ATTN: AMCPM-TVH WARREN MI 40397-5000	1	CDR TRADOC COMBINED ARMS TEST ACTIVITY ATTN: ATCT-CA FORT HOOD TX 76544	1
CDR US ARMY DEVELOPMENT AND EMPLOYMENT AGENCY ATTN: MODE-FDD-CSSB FT LEWIS VA 98433-5000	1	CDR US ARMY LEA ATTN: DALO-LEP NEW CUMBERLAND ARMY DEPOT NEW CUMBERLAND PA 17070	1
	1	CDR HQ, EUROPEAN COMMAND ATTN: J4/7-LJPO (LTC WEINER) VAIHINGEN, GE APO NY 09128	1
	1	CDR US ARMY ENGINEER SCHOOL ATTN: ATSE-CD LEONARD WOOD MO 65473-5000	1

CDR
US ARMY EUROPE & SEVENTH ARMY
ATTN: AEAGG-FMD
AEAGD-TE
APO NEW YORK 09403

CDR
US ARMY FOREIGN SCIENCE & TECH
CENTER
ATTN: AIAST-RA-ST3 (MR BUSI)
FEDERAL BLDG
CHARLOTTESVILLE VA 22901

CDR
US ARMY GENERAL MATERIAL &
PETROLEUM ACTIVITY
ATTN: STRGP-PW
BLDG 247, DEFENSE DEPOT TRACY
TRACY CA 95376-5051

CDR
US ARMY ORDNANCE CENTER &
SCHOOL
ATTN: ATSL-CD-CS
ABERDEEN PROVING GROUND MD
21005-5006

CDR
AMC MATERIEL READINESS SUPPORT
ACTIVITY (MRSA)
ATTN: AMXMD-MO (MR BROWN)
LEXINGTON KY 40511-5101

CDR
101ST AIRBORNE DIVISION (AASLT)
ATTN: AFZB-KE-J
AFSB-KE-DMMC
FORT CAMPBELL KY 42223

TRADOC LIAISON OFFICE
ATTN: ATFE-LO-AV
4300 GOODFELLOW BLVD
ST LOUIS MO 63120-1798

HQ
US ARMY TRAINING & DOCTRINE CMD
ATTN: ATCD-SL-5
FORT MONROE VA 23651-5000

CDR
US ARMY TRANSPORTATION SCHOOL
ATTN: ATSP-CD-MS
FORT EUSTIS VA 23604-5000

1 HQ, US ARMY T&E COMMAND
ATTN: AMSTE-CM-R-O 1
AMSTE-TE-T (MR RITONDO) 1
AMSTE-TA-L (LIVE FIRE OFFICE) 1
1 ABERDEEN PROVING GROUND MD
21005-5006

1 CDR
CONSTRUCTION ENG RSCH LAB
ATTN: CERL-ES 1
P O BOX 4005
CHAMPAIGN IL 61820

1 CDR
US ARMY NATICK RES & DEV CENTER
ATTN: STRNC-U 1
1 NATICK MA 01760-5020

1 CDR
US ARMY QUARTERMASTER SCHOOL
ATTN: ATSM-CDM (MAJ WEIR) 1
ATSM-TD 1
ATSM-PFS (MR ELLIOTT) 1
1 FORT LEE VA 23801

1 DIRECTOR
US ARMY RSCH & TECH ACTIVITIES
(AVSCOM)
PROPELLION DIRECTORATE
ATTN: SAVRT-PL-C (MR ACURIO) 1
1 21000 BROOKPARK ROAD
CLEVELAND OH 44135-3127

1 PROJ MGR, PATRIOT PROJ OFFICE
ATTN: AMCPM-MD-T-C 1
1 U.S. ARMY MISSILE COMMAND
1 REDSTONE ARSENAL AL 35898

1 PROJECT MANAGER
PETROLEUM & WATER LOGISTICS
ATTN: AMCPM-PWL 1
4300 GOODFELLOW BLVD
ST LOUIS MO 63120-1798

1 CDR
US ARMY LOGISTICS CTR
ATTN: ATCL-CD 1
FORT LEE VA 23801-6000

1 CDR
US ARMY FIELD ARTILLERY SCHOOL
ATTN: ATSF-CD 1
FORT SILL OK 73503-5600

HQ, US ARMY ARMOR CENTER ATTN: ATSB-CD-ML (1LT NEALLY) ATSB-TSM-T (MAJ GROSS) FORT KNOX KY 40121	1	CDR US ARMY WESTERN COMMAND ATTN: APLG-TR FORT SCHAFTER HI 96858-5100	1
CDR COMBINED ARMS COMBAT DEVELOPMENT ACTIVITY ATTN: ATZL-CAT-E ATZL-CAT-A FORT LEAVENWORTH KS 66027-5300	1	CDR NAVAL AIR PROPULSION CENTER ATTN: PE-33 (MR D'ORAZIO) PE-32 (MR MANGIONE) P O BOX 7176 TRENTON NJ 06828-0176	1
CDR US ARMY INFANTRY SCHOOL ATTN: ATSH-CD-MS-M FORT BENNING GA 31905-5400	1	CDR NAVAL SEA SYSTEMS COMMAND ATTN: CODE 05M32 WASHINGTON DC 20362-5101	1
DIR US ARMY MATERIALS TECHNOLOGY LABORATORY ATTN: SLCMT-M SLCMT-MCM-P (DR FOPIANO) WATERTOWN MA 02172-2796	1	CDR NAVAL AIR ENGR CENTER ATTN: CODE 92727 LAKEHURST NJ 08733	1
CDR US ARMY ARMOR & ENGINEER BOARD ATTN: ATZK-AE-AR FORT KNOX KY 40121	1	CDR NAVAL SHIP SYS ENGINEERING CTR ATTN: CODE 053C PHILADELPHIA PA 19112-5083	1
CHIEF US ARMY LOGISTICS ASSISTANCE OFC. LAO-CONUS ATTN: AMXLA-CO FORT MCPHERSON GA 30330-6000	1	JOINT OIL ANALYSIS PROGRAM - TECHNICAL SUPPORT CTR BLDG 780 NAVAL AIR STATION PENSACOLA FL 32508-5300	1
CDR US ARMY MEDICAL R&D LABORATORY ATTN: SG RD-USG-M (MR EATON) FORT DETRICK, MD 21701	1	CDR DAVID TAYLOR RESEARCH CTR ATTN: CODE 2830 (MR SINGERMAN) CODE 2759 (MR STRUCKO) CODE 2831 ANNAPOLIS MD 21402-5067	1
CDR US ARMY AVIATION CTR & FT RUCKER ATTN: ATZQ-DI FORT RUCKER AL 36362	1	PROJ MGR, M60 TANK DEVELOPMENT ATTN: USMC-LNO US ARMY TANK-AUTOMOTIVE COMMAND (TACOM) WARREN MI 48397-5000	1
CDR US ARMY SAFETY CENTER ATTN: PESC-SSD FORT RUCKER AL 36362	1	CDR NAVAL RESEARCH LABORATORY ATTN: CODE 6170 CODE 6180 WASHINGTON DC 20375-5000	1
CDR MILITARY TRAFFIC MANAGEMENT CMD ATTN: MT-SA (MR DOWD) WASHINGTON DC 20315	1		

CDR
NAVAL AIR SYSTEMS COMMAND
ATTN: CODE 53632F (MR MEARS)
WASHINGTON DC 20361-5360

CDR
NAVAL AIR DEVELOPMENT CTR
ATTN: CODE 6061
WARMINSTER PA 18974-5000

CDR
NAVAL FACILITIES ENGR CTR
ATTN: CODE 1202B (MR R BURRIS)
200 STOVAL ST
ALEXANDRIA VA 22322

DEPUTY COMMANDING GENERAL
US MARINE CORPS RD&A COMMAND
ATTN: CBAL
QUANTICO VA 22134-5080

CDR
NAVY PETROLEUM OFFICE
ATTN: CODE 43 (MR LONG)
CAMERON STATION
ALEXANDRIA VA 22304-6180

OFFICE OF THE CHIEF OF NAVAL
RESEARCH
ATTN: OCNR-126 (DR ROBERTS)
ARLINGTON VA 22217-5000

CG
FLEET MARINE FORCE PACIFIC
ATTN: G4
CAMP HM SMITH HI 96861

CG
FLEET MARINE FORCE ATLANTIC
ATTN: G4
NORFOLK VA 23511

DEPUTY CG
USMC RDEA COMMAND
ATTN: CBAT (LTC KEPHART)
QUANTICO VA 22134

DEPARTMENT OF THE AIR FORCE

HQ, USAF
ATTN: LEYSF
WASHINGTON DC 20330

CDR
USAF 3902 TRANSPORTATION SQUADRON
ATTN: LGTVP (MR VAUGHN) 1
OFFUTT AIR FORCE BASE NE 68113

CDR
US AIR FORCE WRIGHT AERO LAB
ATTN: AFWAL/POSF (MR DELANEY) 1
AFWAL/POS (MR JONES) 1
AFWAL/MLSE 1
AFWAL/MLBT (MR SNYDER) 1
WRIGHT-PATTERSON AFB OH
45433-6563

CDR
SAN ANTONIO AIR LOGISTICS CTR
ATTN: SAALC/SFT (MR MAKRIS) 1
SAALC/MMPRR 1
KELLY AIR FORCE BASE TX 78241

CDR
DET 29
ATTN: SA-ALC/SFM 1
CAMERON STATION
ALEXANDRIA VA 22304-6179

HQ AIR FORCE SYSTEMS COMMAND
ATTN: AFSC/DLF (DR DUES) 1
ANDREWS AFB MD 20334

CDR
WARNER ROBINS AIR LOGISTIC CTR
ATTN: WRALC/MMTV (MR GRAHAM) 1
ROBINS AFB GA 31098

OTHER GOVERNMENT AGENCIES

NATIONAL AERONAUTICS AND SPACE
ADMINISTRATION 1
LEWIS RESEARCH CENTER
CLEVELAND OH 44135

ENVIRONMENTAL PROTECTION AGENCY
AIR POLLUTION CONTROL 1
2565 PLYMOUTH ROAD
ANN ARBOR MI 48105

DEPARTMENT OF TRANSPORTATION
FEDERAL AVIATION ADMINISTRATION
ATTN: AWS-110 1
800 INDEPENDENCE AVE, SW
WASHINGTON DC 20590

US DEPARTMENT OF ENERGY
ATTN: MR ECKLUND
MAIL CODE CE-151
FORRESTAL BLDG.
1000 INDEPENDENCE AVE, SW
WASHINGTON DC 20585

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